



## Novel Coumarin Substituted Cu (II) and Cu (II) Phthalocyanines: Preparing, Researching Spectroscopic Properties and Molecular Modeling

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The original Cu (II) and Co (II) metallo phthalocyanine complexes substituted with 7-oxy-4-(pyridin-3-yl)coumarin moieties both in peripheral and non-peripheral positions were synthesized and their structure characterized. Their electronic absorption spectra and aggregation properties were investigated in DMF and DMSO. The Cu metallo peripheral substituted phthalocyanine complex was exhibited an aggregation band in both DMF and DMSO. On the other phthalocyanine complexes no aggregation band was observed. Optimized geometry of the molecules was drawn using Gauss-View 5 program, and their state at lowest energy was determined using Gaussian 09 program. However, energy-minimized structure, electronic distribution and molecular orbitals were obtained by DFT/B3LYP/6-31G (d,p) calculations which were supported by experimental results.

Keywords: Metallo phthalocyanine, DFT, coumarin.

### Introduction

Phthalocyanines (Pcs) are organic heterocyclic complexes which are important as a group of molecular functional materials.<sup>1,2</sup> Pcs and their derivatives have a rich and various coordination chemistry, based on the structure of the substituent and large diversity of compounds formed with most of the elements in the periodic table.<sup>3,4</sup> They are interesting complexes because of their high stability, excellent spectroscopic characteristics and electrical conductivity. They have great utilizations like photodynamic therapy, nonlinear optical materials, optical recording materials, catalysis, and chemical sensors.<sup>5-8</sup>

Coumarins (2H-chromen-2-one) are a kinds of organic matters that are ubiquitous in numerous native products, pharmaceuticals,

dyes, and material science.<sup>9,10</sup> Coumarin has a great quantum yield, important photo-stability, and superior fluorescence in visible light.<sup>11,12</sup> Pyridyl substituted coumarin compounds have interesting chemical, photophysical, and spectroscopic properties.<sup>13-15</sup> Therefore we proposed that the incorporation of the pyridyl substituted coumarin onto the Pc skeleton can give rise to a change in the spectroscopic activities of the main compounds.

In the present study, we have synthesized metallo Pcs bearing coumarin moiety in order to explore better spectroscopic properties and novel characteristics to be used for specific areas. After synthesizing two new phthalonitrile compounds (1 and 2), Cu (II) and Co (II) metallo Pc complexes (1a-b, 2a-b) were prepared. Spectroscopic characteristics and

aggregation behaviour of Pc complexes were researched and compared in DMSO and DMF. In recent years, the density functional theory (DFT) based on the methods have become very popular. Best DFT methods, requires less power from conventional correlation techniques. This study optimized geometries draw with Gaussian calculations was made in Gaussian 09 View 5 software package.<sup>16</sup> DFT method is used in the program. Cu (II) and Co (II) metallo Pc complexes (1a-b, 2a-b) are drawn through Gauss-View 5 program on the computer. Then, Gaussian 09 program were made geometric optimization of the lowest energy state.

## Experimental

### Materials and equipment

Potassium carbonate ( $K_2CO_3$ ) were acquired from Merck. Copper (II) chloride ( $CuCl_2$ ) and cobalt (II) chloride ( $CoCl_2$ ) were purchased of Sigma-Aldrich. Hexan-1-ol, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were dried by noticed procedures<sup>17</sup> before use. Nitrile ligands (**1** and **2**) were prepared by literature method.<sup>18</sup> Shimadzu UV-2600 UV-vis spectrophotometer was utilized to get of electronic spectrum of new Pcs. Infrared spectra were obtained on Perkin-Elmer FT-IR Spectrum One spectrophotometers. Mass spectra were acquired on a Bruker Microflex LT MALDI-TOF spectrometer (matrix: dithranol / DIT).

### Theoretical calculations

TD-DFT calculations methods used precise electron density to calculate molecular properties and energies, taking into account electron correlation. DFT calculations were performed by the Lee-Yang-Parr correlation functional hybrid B3LYP.

In such calculations, it is the 6-31G(d) basis set that is used.<sup>16</sup> Vibration frequencies

were calculated to determine the potential energy surfaces of the structures as fixed points and real minimums. All possible fixed geometries found at minimum are formed by free rotation around single bonds.<sup>19</sup> This electronic structure provides state of the art capabilities for modeling. Gaussian 09 is a considerably comprehensive program, which includes molecular mechanics, semi-empiric, and ab initio methods. The program has a wide range of theory and basic set options for the three methods. With the Gaussian 09 program, the energies of atoms and molecules can be calculated, geometric optimizations can be made, and energy dependent vibration frequencies, force constants, and dipole moments can be calculated. The program can navigate potential energy surfaces and scan minima, transition states and reaction pathways. The program can also test the stability of the molecular wave function.

### Synthesis

#### *The synthesis of Pcs (1a-b, 2a-b)*

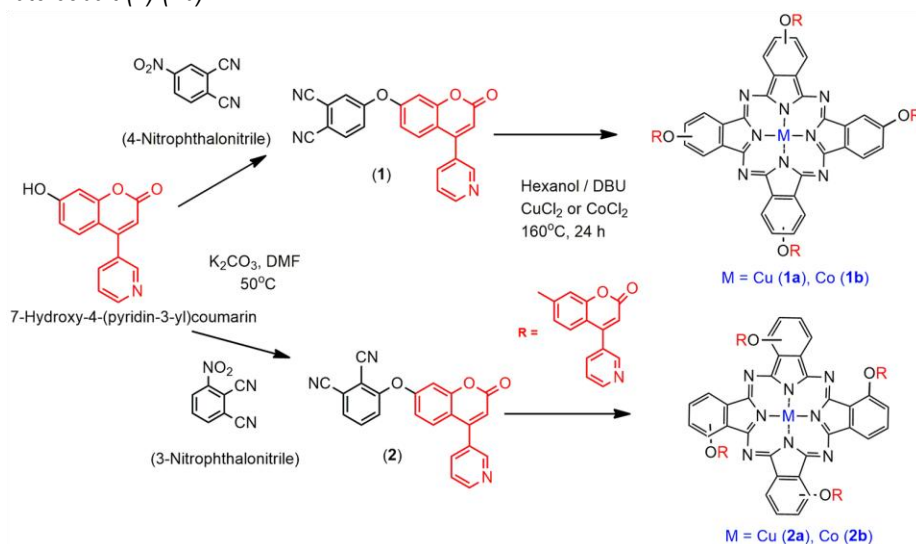
A blend of nitrile ligand **1** or **2** (0.10 g, 0.27 mmol), 0.069 mmol metal chlorides ( $CuCl_2$  0.0092 g or  $CoCl_2$  0.0089 g) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (10  $\mu$ L) in dried hexan-1-ol (1.0 mL) was refluxed for a day. Then, ethyl alcohol was added onto the mixture to precipitate the green or blue product. The residues were rinsed out several times with acetonitrile, ethyl acetate, tetrahydrofuran, methanol and acetone as to extracted the any solvable waste products. The product was also purged by solving it in DMF and then precipitating with hot acetone for a few times.

*2(3),9(10),16(17),23(24)-Tetrakis[4-(2-oxo-4-(pyridin-3-yl)-2H-chromen-7-yloxy)]  
phthalocyaninato copper (II) (1a):*

Green-blue powder. mp>300 °C; FT-IR:  $\nu$  3065-2990 (Ar-CH), 1720 (C=O), 1620 (C=C), 1570 (C=N), 1560–1470 (aryl C=C), 1258 (Ar-O-Ar), 1150 (Ar-O-C)  $\text{cm}^{-1}$ . UV (DMF),  $\lambda$  (nm) (log  $\epsilon$ ): 672 (4.76), 614 (4.85), 333 (5.12); Anal. calculated for  $\text{C}_{88}\text{H}_{44}\text{N}_{12}\text{O}_{12}\text{Cu}$ : C, 69.31; H, 2.89; N, 11.03. Found: C, 69.33; H, 2.86; N, 11.10. MS (MALDI-TOF)  $m/z$ : calculated for  $[\text{C}_{88}\text{H}_{44}\text{N}_{12}\text{O}_{12}\text{Cu}]^+$ : 1523.5008. Found: 1523.1032  $[\text{M}]^+$ .

(3),9(10),16(17),23(24)-Tetrakis[4-(2-oxo-4-(pyridin-3-yl)-2H-chromen-7-yloxy)]phthalocyaninato cobalt (II) (1b):

Green-blue powder. mp>300 °C; FT-IR:  $\nu$  3070-2985 (Ar-CH), 1717 (C=O), 1610 (C=C), 1580 (C=N), 1575–1465 (aryl C=C), 1260 (Ar-O-Ar), 1163 (Ar-O-C)  $\text{cm}^{-1}$ . UV (DMF),  $\lambda$  (nm) (log  $\epsilon$ ): 665 (4.41), 326 (4.73); Anal. calculated for  $\text{C}_{88}\text{H}_{44}\text{N}_{12}\text{O}_{12}\text{Co}$ : C, 69.51; H, 2.90; N, 11.06. Found: C, 69.54; H, 2.88; N, 11.02. MS (MALDI-TOF)  $m/z$ : calculated for  $[\text{C}_{88}\text{H}_{44}\text{N}_{12}\text{O}_{12}\text{Co}]^+$ : 1519.1812. Found: 1519.6031  $[\text{M}]^+$ .



**Scheme 1.** Synthesis of nitrile ligands (1, 2) and coumarin substituted Pcs (1a-b, 2a-b).

1(4),8(11),15(18),22(25)-Tetrakis[3-(2-oxo-4-(pyridin-3-yl)-2H-chromen-7-yloxy)]phthalocyaninato copper (II) (2a):

Green-blue powder. mp>300 °C; FT-IR:  $\nu$  3080-2990 (aryl -CH), 1710 (C=O), 1610 (C=C), 1582 (C=N), 1564–1462 (aryl C=C), 1275 (aryl-O-aryl), 1184 (aryl-O-C)  $\text{cm}^{-1}$ . UV (DMF),  $\lambda$  (nm) (log  $\epsilon$ ): 690 (5.05), 330 (4.79); Anal. calculated for  $\text{C}_{88}\text{H}_{44}\text{N}_{12}\text{O}_{12}\text{Cu}$ : C, 69.31; H, 2.89; N, 11.03. Found: C, 69.28; H, 2.93; N, 11.05. MS (MALDI-TOF)  $m/z$ : calculated for

$[\text{C}_{88}\text{H}_{44}\text{N}_{12}\text{O}_{12}\text{Cu}]^+$ : 1523.5008. Found: 1523.7105  $[\text{M}]^+$ .

1(4),8(11),15(18),22(25)-Tetrakis[3-(2-oxo-4-(pyridin-3-yl)-2H-chromen-7-yloxy)]phthalocyaninato cobalt (II) (2b):

Green-blue powder. mp>300 °C; FT-IR:  $\nu$  3065-2990 (aryl -CH), 1713 (C=O), 1617 (C=C), 1585 (C=N), 1572–1465 (aryl C=C), 1261 (aryl-O-aryl), 1176 (aryl-O-C)  $\text{cm}^{-1}$ . UV (DMF),  $\lambda$  (nm) (log  $\epsilon$ ): 675 (4.64), 328 (4.82); Anal. calculated for  $\text{C}_{88}\text{H}_{44}\text{N}_{12}\text{O}_{12}\text{Co}$ : C, 69.51; H, 2.90; N, 11.06. Found: C, 69.49; H, 2.93; N,

11.12. MS (MALDI-TOF)  $m/z$ : calculated for  $[C_{88}H_{44}N_{12}O_{12}Co]^+$ : 1519.1812. Found: 1519.5404  $[M]^+$ .

## Results and discussion

### Synthesis and characterization

Scheme 1 demonstrates the general synthesis paths of the new nitrile ligands (1, 2), Cu (II) and Co (II) metallated Pcs (1a-b, 2a-b). Nitrile ligands (1 and 2) were prepared by literature method.<sup>18</sup> Cu (II) and Co (II) Pcs (1a-b, 2a-b) were prepared in the following way: metal salts ( $CuCl_2$  or  $CoCl_2$ ), DBU and ligands (1 or 2) were heated in dried hexan-1-ol at 160°C. The novel Pcs were defined by FT-IR and MALDI-TOF techniques. All spectroscopic info were suitable with the estimated structure of the Pcs.

Ligands (1 and 2) and Pc complexes (1a-b and 2a-b) have similar FT-IR spectra except the  $\nu(C\equiv N)$  vibrations.  $^1H$  NMR measurement was precluded for the 1a-b and 2a-b owing to their paramagnetic nature. Molecular ions were certainly noticed at  $m/z$ : 1523.1032  $[M]^+$  for 1a, 1519.6031  $[M]^+$  for 1b (Fig 1), 1523.7105  $[M]^+$  for 2a and 1519.5404  $[M]^+$  for 2b and the mass results of Pcs (1a-b and 2a-b) approved the suggested structures.

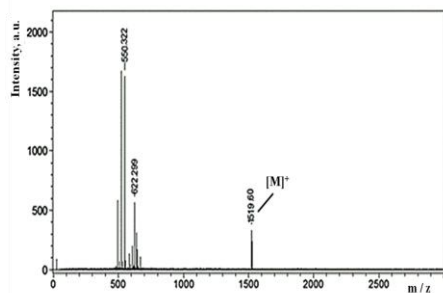


Fig. 1. MALDI-TOF spectrum of complex 1b.

### Electronic absorption spectra

Cu, Co metallo Pc complexes both in peripheral (1a and 1b) and non-peripheral (2a and 2b) positions were displayed typical Q and

B band absorptions in the electronic spectra (Fig 2). Q band absorptions formed by  $\pi-\pi^*$  transitions were seen at 672 (1a), 665 (1b), 690 (2a) and 675 nm (2b) in DMF, Table 1. Pc complexes substituted in non-peripheral positions (2a and 2b) showed bathochromic shift relative to peripherally Pc complexes in DMF: 18 nm (between 1a - 2a) and 10 nm (between 1b - 2b). Non-peripheral Pc complexes causes  $\pi^*$ -orbital energy absorption reduces variations across longer wavelengths.<sup>20,21</sup> In the UV-vis spectra of Pcs, the B bands were viewed at 333 nm (1a), 326 nm (1b), 330 nm (2a) and 328 nm (2b).

The aggregation properties of Pcs (1a-b and 2a-b) were researched in DMF at various concentrations (Fig 2). Q band intensity was also increased, with the increase in concentration and new band was not formed due to aggregation except complex 1a. All Pc complexes were adhered to the Beer-Lambert rule in the  $1.2 \times 10^{-5}$  to  $2 \times 10^{-6}$  M concentration range. However, aggregation in complex 1a was emerged with a split and broadened the Q band. Division of the Q band of 1a (for monomer at 672 nm and for aggregate at 618 nm) was sign of aggregation consisting inside of solution. When the spectrum taken in DMSO, the aggregation band is more pronounced from the monomer band for complex 1a. This aggregation type, is an indication of H type aggregation genesis. This genesis is simply identified from blue shift and widen of their Q band absorption.<sup>22</sup> Depending on the supramolecular system, the wavelength corresponding to the maxima of the absorption bands of the H aggregates of the Pcs ranges from 580 to 630 nm.<sup>23</sup> In the case of non-peripheral substituted Cu (II) Pc complex (2a), no aggregation band was observed in DMF and DMSO (Fig 3). Peripheral substitution on

Pcs have a powerful trend to aggregate and display a wide Q band than the non-peripheral substitution on Pc derivatives.<sup>24,25</sup> No aggregation band was observed for Co (II) Pc complexes (1b and 2b) in both DMF or DMSO.

*Computational results*

Computational properties of Cu (II) and Co (II) metallo Pc complexes (1a-b, 2a-b), the optimized molecular structure was first obtained by DFT calculations in the gas phase (Fig 4). Also, based on the results of the

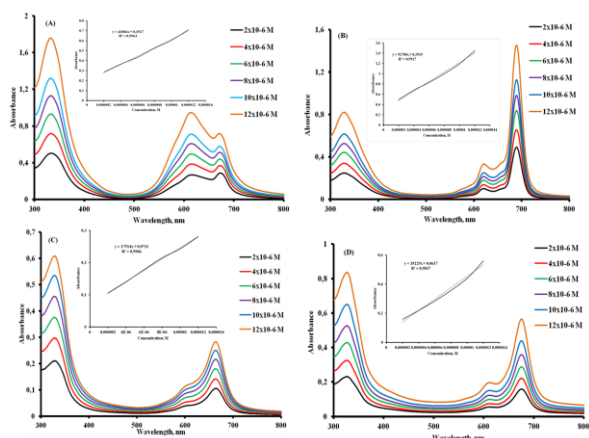
optimized geometry frequency calculations, virtual frequency supports minimal success towards non-observation geometry optimization. The calculations of Mulliken atom Cu charge (0.718 and 0.722) (1a, 2a) and Co (1b, 2b) (0.815 and 0.823) are appropriate for the covalent nature of the metal ligand bond. Table 2 is in the Mulliken populations and the atomic charge show. 1a, 1b, 2a and 2b DFT were calculated at the same level. HOMO and LUMO energy grades are shown in Fig 5.

**Table 1.** Absorption values of Pcs (1a-b, 2a-b) in DMF fragments(  $1 \times 10^{-5}$  M)

Complex	B band (nm)	log $\epsilon$	Q band (nm)	log $\epsilon$
<b>1a</b>	333	5.12	672	4.76
<b>1b</b>	326	4.73	665	4.45
<b>2a</b>	330	4.79	690	5.05
<b>2b</b>	328	4.82	675	4.64

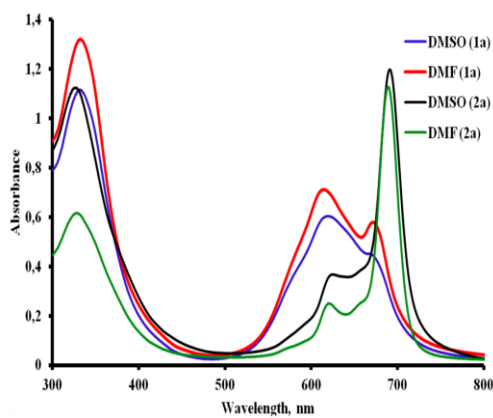
**Table 2.** Mulliken loads of studied

Cu (1a)	Co (1b)	Cu (2a)	Co (2b)
Cu <sub>39</sub> 0.718	Co <sub>157</sub> 0.815	Cu <sub>12</sub> 0.722	Co <sub>49</sub> 0.823
N <sub>1</sub> -0.356	N <sub>1</sub> -0.422	N <sub>1</sub> -0.344	N <sub>1</sub> -0.425
N <sub>78</sub> -0.415	N <sub>77</sub> -0.345	N <sub>24</sub> -0.420	N <sub>23</sub> -0.344
N <sub>155</sub> -0.010	N <sub>155</sub> -0.022	N <sub>123</sub> -0.014	N <sub>124</sub> -0.020
O <sub>13</sub> -0.543	O <sub>13</sub> -0.432	O <sub>50</sub> -0.550	O <sub>76</sub> -0.437
O <sub>89</sub> -0.823	O <sub>88</sub> -0.714	O <sub>102</sub> -0.825	O <sub>130</sub> -0.725

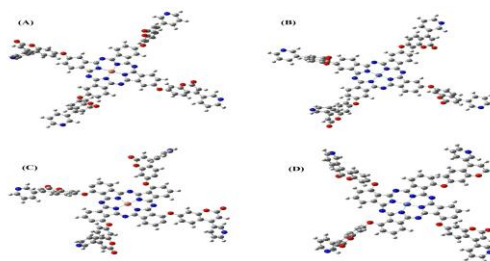


**Fig. 2.** Absorption spectra of (A) 1a, (B) 2a, (C) 1b and (D) 2b in DMF.

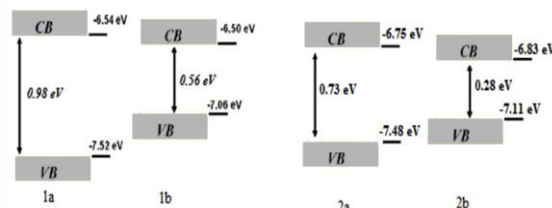
The new phthalonitriles (1 and 2) and Cu, Co metallo Pc complexes both in peripheral (1a and 1b) and non-peripheral (2a and 2b) positions were synthesized. Evidence of the structures of all prepared novel compounds was obtained by MALDI-TOF and FT-IR spectroscopic techniques.



**Fig. 3.** Absorption spectra of copper metallo Pcs (1a, 2a) in DMF and DMSO ( $1 \times 10^{-5}$  M).



**Fig. 4.** Optimized structures of (A) Pc 1a, (B) Pc 1b, (C) Pc 2a and (D) Pc 2b, the numbering system (gray, C; red, O; blue, N; white, H; puppies mouth, Cu; light blue, Co).



**Fig. 5.** Electronic structures of the Pcs 1a, 1b, 2a and 2b computed with DFT/B3LYP method.

### Conclusion

Absorption spectra of the Pcs were detected using DMF and DMSO solvents. The results of the absorption spectra showed typical Pc behaviour for the all Pc complexes. The peripherally substituted CuPc (1a) was exposed an aggregation band at 618 nm in while its non-peripheral derivative (2a) no aggregation band was observed in DMF and DMSO. In DFT and TD-DFT (vacuum state), the analysis of the electrostatic surface potential suggested electronegativity found in the nitro group. Finally, based on the experimental results along with the DFT calculations, one can be said of (1a, 1b, 2a and 2b) due to the input of additional electronic states in the band gap. In addition, spectroscopic and electronic properties (1a, 1b, 2a and 2b) were studied with computer

work and the results were consistent with the experiment.

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